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Continuous Monoglyceride Production from Palm Fatty Acid Distillate and Glycerol Using Vacuum Reactive Distillation Column

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***Abstract*— This paper focused on the simulation-based study using Aspen Plus Ver. 7.2 to evaluate possible flow diagram processes and process configurations related to the continuous production of monoglyceride from palm fatty acid distillate-glycerol esterification using strong acidic cation resin in a reactive distillation column. Basic operating conditions evaluated was the operating pressure. Evaluation between atmospheric and vacuum operating pressure showed that the latter could give better product quality by avoiding the product from cracking or destructed due to too high operating temperature when the operating pressure was atmospheric (1 bar). The preferred vacuum pressure was 0.05 bar which resulted in the maximum temperature at the bottom stream of distillation column was about 335^{o}C, lower than a maximum allowable temperature which was 350^{o}C. On the other hand, atmospheric condition resulted in maximum temperature at the stream was about 520^{o}C. Afterward, two scenarios were evaluated which were using one reactive distillation column with high reboiler duty combined with only one distillation column (Scenario-1) or using one reactive distillation column with moderate reboiler duty combined with two distillation columns (Scenario-2) to have high purity monoglycerides. Scenario-2 showed a little bit more sophisticated flowsheetings but yielded in less overall energy consumption for relatively the same monoglycerides purity at the bottom stream of the distillation column.**

***Keywords*— Reactive distillation; palm fatty acid distillate; monoglyceride; vacuum distillation; ASPEN Simulation**

I. INTRODUCTION

Recently, monoglycerides presented as one of the most wanted products derived from free fatty acids [1], [2], [3]. On the other hand, the current interesting fatty acid source was palm fatty acid distillate (PFAD). The PFAD was the byproduct of crude palm oil (CPO) physical refining with the amount of 3.66 ton/100 ton CPO produced [4], [5] composed of linoleic acid and oleic acid as the major components [6], [7].

Most of the studies related to monoglyceride production through PFAD esterification with glycerol were experimental-based and laboratory scale. Meanwhile, to fulfill the market demand and to have aggressive supply, monoglyceride production must be conducted continuously and in industrial scale. Therefore, this work tried to identify the most optimum process configuration and condition to have the process economically feasible. Since water presented as the byproduct of esterification process, one thing to be considered was how to remove the water easily from the reaction mixture in the continuous process. Fortunately, previous work by Poddar et al. [8], Wu et al. [9], and Singha et al. [10] showed that fatty acid esterification could be combined with the separation process using reactive distillation column.

The approach used in this study was simulation-based. The simulation-based approach provides such advantages that cost and time to conduct real continuous experiment could be managed efficiently by identifying the "do's and don'ts" related to the process condition and configuration during the experiment [11]. The simulation conducted in this work focused on the selection of the best flow diagram process and its configuration by focusing on both product purity and energy consumption by each option.

II. MATERIALS AND METHODS

Since this reaction was considered as a heterogeneous reaction, there were two capable reaction mechanisms to describe the phenomenon, which were Langmuir – Hinshelwood, and Eley – Rideal. The previous study by Sudibyo et al. [6] suggested that heterogeneous esterification of PFAD and glycerol were best carried out using Langmuir-

Hinshelwood mechanism. The esterification reaction pathways for the PFAD components were described in Eq. 1 – Eq. 6. As stated in Eq. 1 – Eq. 6, the reactions were irreversible towards the product. This assumption was acceptable because the water was removed using xylene-based reflux system [3].

$$\text{Linoleic acid} + \text{Glycerol} \rightarrow \text{Monolinolein} + H_2O \quad (1)$$

$$\text{Linoleic acid} + \text{Monolinolein} \rightarrow \text{Dilinolein} + H_2O \quad (2)$$

$$\text{Linoleic acid} + \text{Dilinolein} \rightarrow \text{Trilinolein} + H_2O \quad (3)$$

$$\text{Oleic acid} + \text{Glycerol} \rightarrow \text{Monoolein} + H_2O \quad (4)$$

$$\text{Oleic acid} + \text{Monoolein} \rightarrow \text{Diolein} + H_2O \quad (5)$$

$$\text{Oleic acid} + \text{Diolein} \rightarrow \text{Triolein} + H_2O \quad (6)$$

The data obtained from the batch experiment was then transferred into continuous process simulation. The simulations were conducted using chemical process design software simulator, Aspen Plus Ver. 7.2.

The simulation aimed to predict continuous process performance of PFAD-glycerol esterification in various operating conditions as well as determining the feasible alternatives to obtain high purity product. In the ASPEN simulation, the rate of reaction equations (including its kinetics constants value) adopted from Sudibyo et al. [6] still needed to be modified into Power Law form as written in Eq. 7 – Eq. 12.

$$-r_2 = \frac{k_{r2}}{K_G^2}.C_L.C_{ML}.C_G^{-2} = k_2'.C_L.C_{ML}.C_G^{-2} \quad (7)$$

$$-r_3 = \frac{k_{r3}}{K_G^2}.C_L.C_{DL}.C_G^{-2} = k_3'.C_L.C_{DL}.C_G^{-2} \quad (8)$$

$$-r_4 = \frac{k_{r4}}{K_G^2}.C_O.C_G^{-1} = k_4'.C_O.C_G^{-1} \quad (9)$$

$$-r_1 = \frac{k_{r1}}{K_G^2}.C_L.C_G^{-1} = k_1'.C_L.C_G^{-1} \quad (10)$$

$$-r_5 = \frac{k_{r5}}{K_G^2}.C_O.C_{MO}.C_G^{-2} = k_5'.C_O.C_{MO}.C_G^{-2} \quad (11)$$

$$-r_6 = \frac{k_{r6}}{K_G^2}.C_O.C_{DO}.C_G^{-2} = k_6'.C_O.C_{DO}.C_G^{-2} \quad (12)$$

The Power Law form in Eq. 7 – Eq. 12 assumed that there was a molar excess of glycerol used as a reactant. In this study, the molar ratio of PFAD and glycerol used was 1:3. By adapting the reaction kinetics constants value obtained from the previous study by Sudibyo et al. [6], new reaction kinetics constants value related to the Power Law form (Eq. 7 – Eq. 12) were obtained and was shown in Table 1.

In the simulation, reactive distillation was performed within *Radfrac* model. The *Radfrac* model was selected due to its capability in performing the rigorous calculation of mass balance, enthalpy balance and phase equilibrium for the vapour-liquid system. Appropriate property method should be chosen carefully in order to obtain reliable results. The *UNIQUAC* model was selected as the property method to perform the simulation as it was also suggested by Bhatia et al. [12], Banchero et al. [13], and Lazzus [14]. Beside the *Radfrac* model and *UNIQUAC* property method, other process equipment models such as *DSTWU* column, heater, mixer and heat exchanger were also considered for estimating the most suitable system configuration. Reaction kinetics constants from Table 1 were used to proceed the *Radfrac* simulation of reactive stages. Vacuum operating pressure was preferred to start the simulation in the purpose of finding the best-operating conditions since the boiling point of the involving components were very high. Several key parameters were first determined to run basic reactive distillation simulation. The parameters were shown in Table 2.

Aspen Plus Ver. 7.2 had provided the relatively vast component database. However, for components which were not contained in the database, new basic data needed to be supplied into the simulation. In this step, the molecular structures of monolinolein, monoolein, dilinolein, diolein, trilinolein, and triolein were supplied to the simulation by drawing the molecular structure. Physical and chemical properties of the aforementioned components were then calculated by the simulator based on chemical bonds and the corresponding atoms.

Before proceeded into the calculation, the diameter of the reactive distillation column must be calculated. The calculation followed Eq. 13 and Eq. 14 [15].

$$\hat{u}_v = (-0.171 l_t^2 + 0.27 l_t - 0.047).\left[\frac{\rho_L - \rho_V}{\rho_V}\right]^{0.5} \quad (13)$$

$$D_C = \sqrt{\frac{4.\dot{V}_w}{\pi.\rho_c.\hat{u}_v}} \quad (14)$$

In this simulation, there were two configurations evaluated. In both scenarios, remaining glycerol was recycled and mixed with fresh glycerol to become warm glycerol feed stream. Relatively high-temperature product stream made it possible to design heat integration within the process. In the simulation, product stream having relatively high temperature was used as heating fluid in the pre-heater (HE-01).

1) Scenario-1: In this scenario, the reactive distillation column was followed by one distillation column to separate glycerol and water. In the reactive distillation column, product and reactant separation was achieved by increasing reboiler duty. The configuration of scenario-1 was shown in Fig. 1.

2) Scenario-2: The scenario-2 used 2 distillation columns after reactive distillation column. The first distillation column (DC-01) was for separating glycerol and water, while the second one (DC-02) was for separating the reaction product and glycerol. Process flow diagram of Scenario-2 was shown in Fig. 2.

TABLE I
REACTION KINETICS CONSTANTS VALUE FOR POWER-LAW-BASED RATE OF REACTION EQUATIONS

Constants	Arrhenius constants	
	A	E, cal/mol
k_1' [mol/(L.min)]	3.10E+05	8,114.91
k_2' [mol/(L.min)]	3.12E+05	18,651.97
k_3' [mol/(L.min)]	6.24E+10	25,012
k_4' [mol/(L.min)]	3.07E+05	8,045.32
k_5' [mol/(L.min)]	2.61E+08	19,998
k_6' [mol/(L.min)]	5.80E+08	30,100

TABLE II
OPERATING CONDITION FOR BASE SIMULATION

Parameter	Value
PFAD flow basis	10 tons/day
Glycerol-PFAD molar ratio	3
Total number of stages	9
Total number of reactive stages	3 (from 4 to 6)
Condenser type (stage 1)	Total
Reboiler type (stage 9)	Kettle

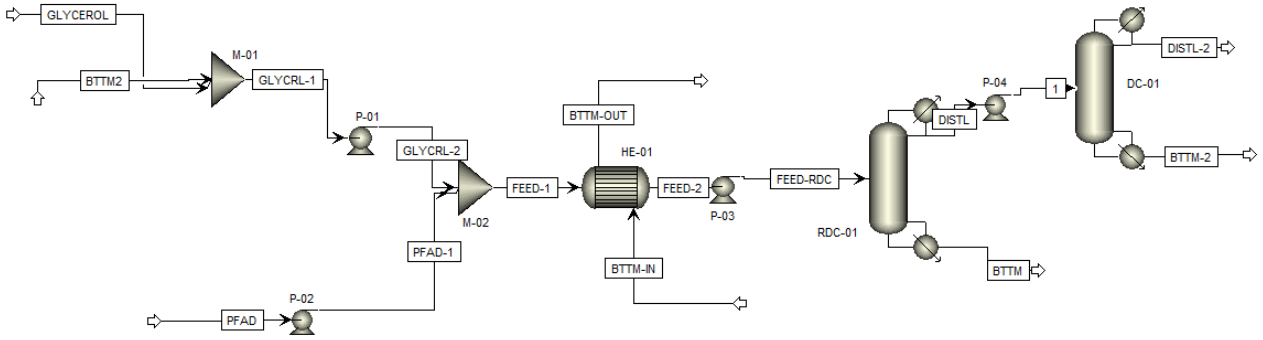

Fig. 1 Scenario-1 process flow diagram

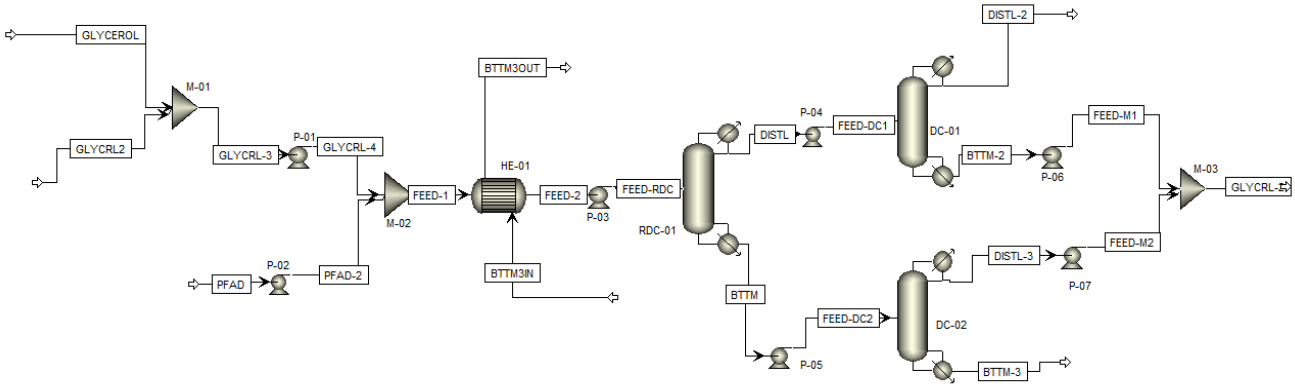

Fig. 2 Scenario-2 process flow diagram

III. RESULTS AND DISCUSSIONS

The diameter of the reactive distillation column was calculated using Eq. 19 by setting the plate spacing of 0.6 m, vapor flow rate of 0.07835 kg/s, liquid phase density of 802.19 kg/m^3, and gas phase density of 0.37 kg/m^3. Afterward, the diameter was calculated using Eq. 14 which resulted in 0.33 meter in diameter.

$$\hat{u}_v = \left(-0.171(0.6)^2 + 0.27(0.6) - 0.047\right).\left[\frac{802.19 - 0.37}{0.37}\right]^{0.5}$$

$$\hat{u}_v = 2.5\ m/s$$

$$D_C = \sqrt{\frac{4(0.07835)}{\pi(802.19)(2.5)}} = 0.33\ \text{m}$$

Correlation between several parameters towards the purity of product could be estimated by utilizing Sensitivity Analysis model analysis tools in Aspen Plus. In this simulation, the reactive distillation column had nine sieve-tray stages which consisted of 3 rectifying stages, 3 reactive stages, and 3 enriching stages. The Fig. 3 showed sensitivity results of product purity as the function of molar reflux ratio, preheater temperature, reboiler duty and feed stage position. Based on Fig. 3 (a), higher reflux ratio resulted in lower product purity in the bottom stream which is represented by monolinolein and monoolein mass fraction. Although glycerol was mostly split into top stream, the increasing reflux ratio obviously caused more glycerol in bottom product thus reducing product purity. In Fig. 3 (b), greater feed temperature enabled the better product purification. In Fig. 3 (c), the increasing reboiler duty became relatively insignificant within the value greater than 0.21 Gcal/hr.

Sensitivity results in Fig. 3 (d) showed that selection of the feed stage relatively close to reboiler would reduce the mass fraction of reaction product (mono-, di-, and tri-glycerides) both in the top stream and in the bottom stream. The reason was, by feeding the feed close to the reboiler, the reactants (PFAD and glycerol) would directly vaporize while the optimum rate of reaction occurred in the liquid phase. All optimum conditions related to those four parameters were marked by a red dashed line in each graph.

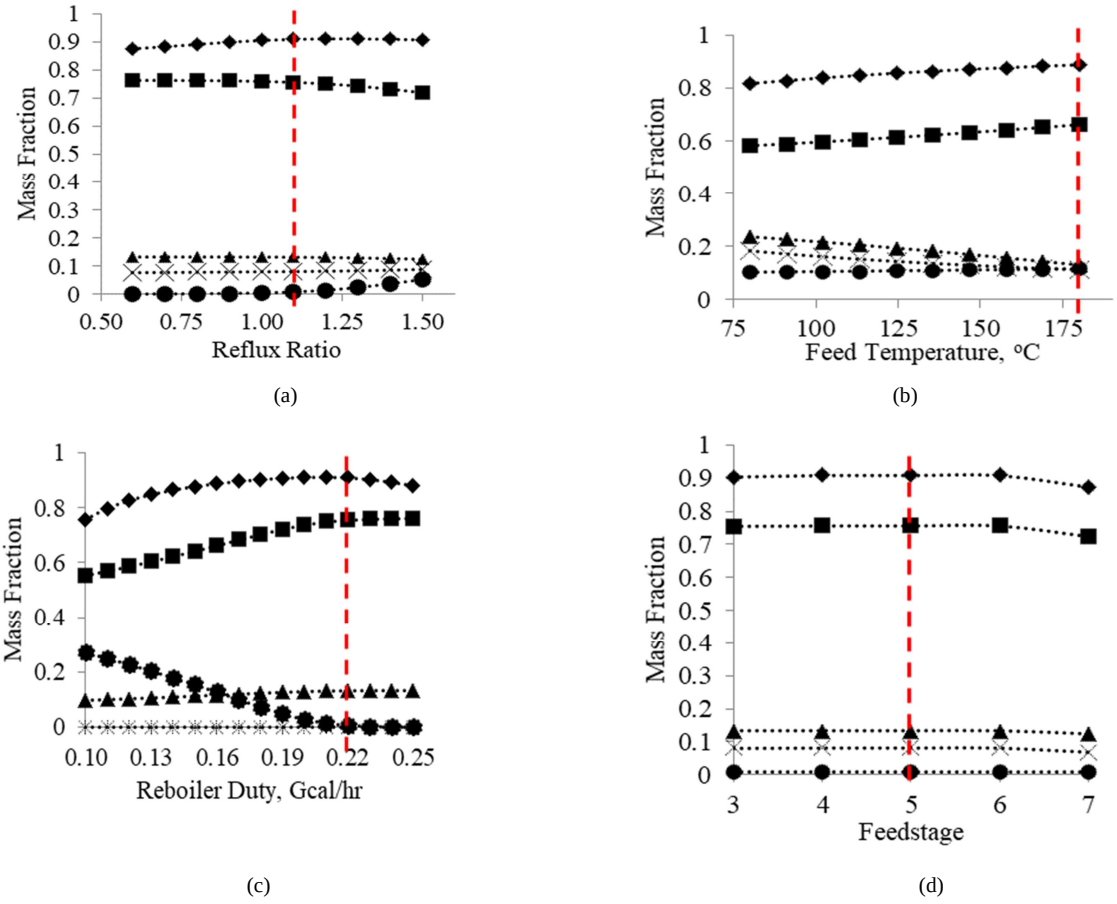

Fig. 3 Profile of column compositions (a). as a function of reflux ratio (b). as a function of heater temperature (c). as a function of reboiler duty (d). as a function of feed stage position with ♦:Glycerol-Top ■: Monolinolein ▲: Monoolein **X**: Water-Top ●: Glycerol-Bottom

TABLE III
CALCULATION RESULTS FOR SCENARIO-1 AND SCENARIO-2 UNDER VACUUM PRESSURE CONDITION

Parameters	**Scenario-1**		**Scenario-2**	
Monolinolein purity	75.2%	FFA	75.4%	FFA
Monoolein purity	13.2%	Conversion:	13.2%	Conversion:
Dilinolein purity	10.4%	99.7%	10.4%	99.8%
Energy consumption	0.327 Gcal/hr		0.293 Gcal/hr	

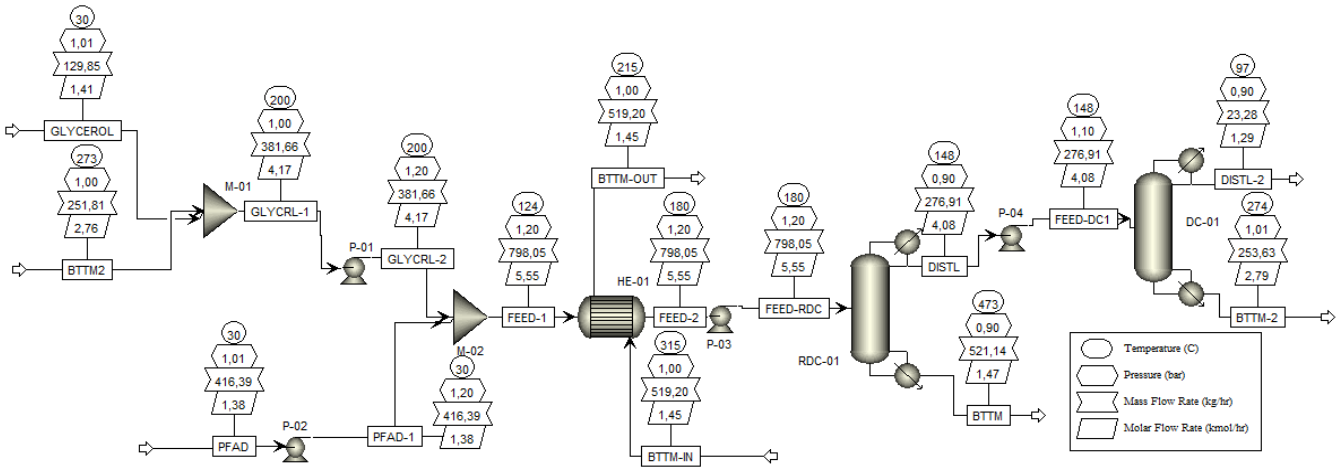

Fig. 4 Calculation result for scenario-1 process flow diagram under atmospheric pressure condition (1 bar)

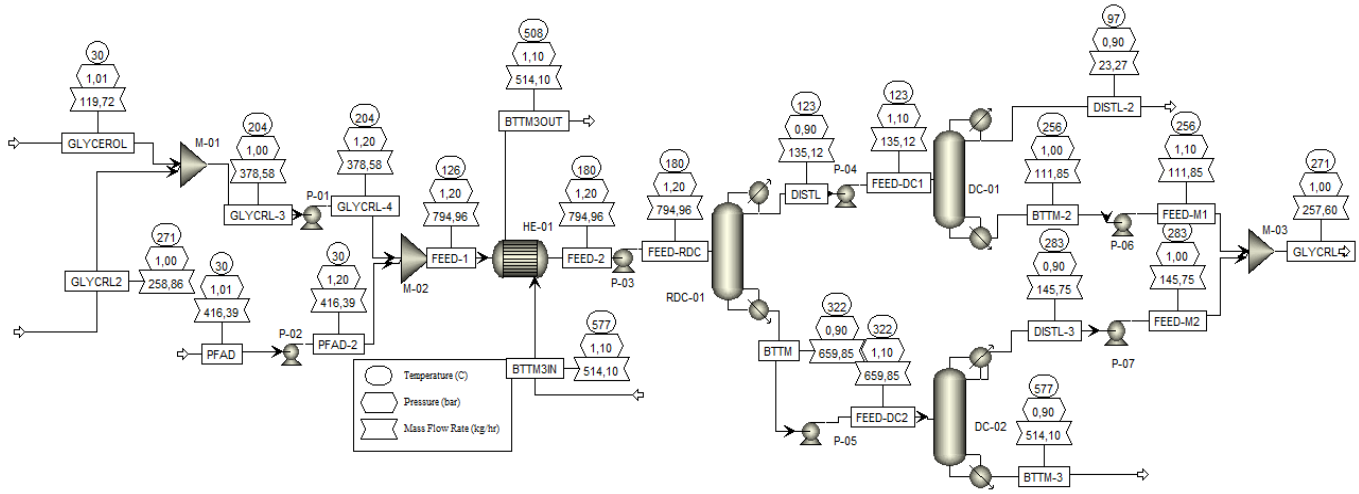

Fig. 5 Calculation result for scenario-2 process flow diagram under atmospheric pressure condition (1 bar)

The Fig. 4 and Fig. 5 stood for atmospheric pressure system in the reactive distillation system. Unfortunately, operating the continuous monoglycerides production under atmospheric pressure condition might lead to the destruction or the cracking of carbon bonding in the reactant and product due to extremely high temperature. From Fig. 4 (the bottom stream of RDC-01) and Fig. 5 (the bottom stream of DC-02), the temperature of the stream was greater than 500^{o}C, much higher than the allowable operating temperature to keep the quality of the product which was 350^{o}C [16].

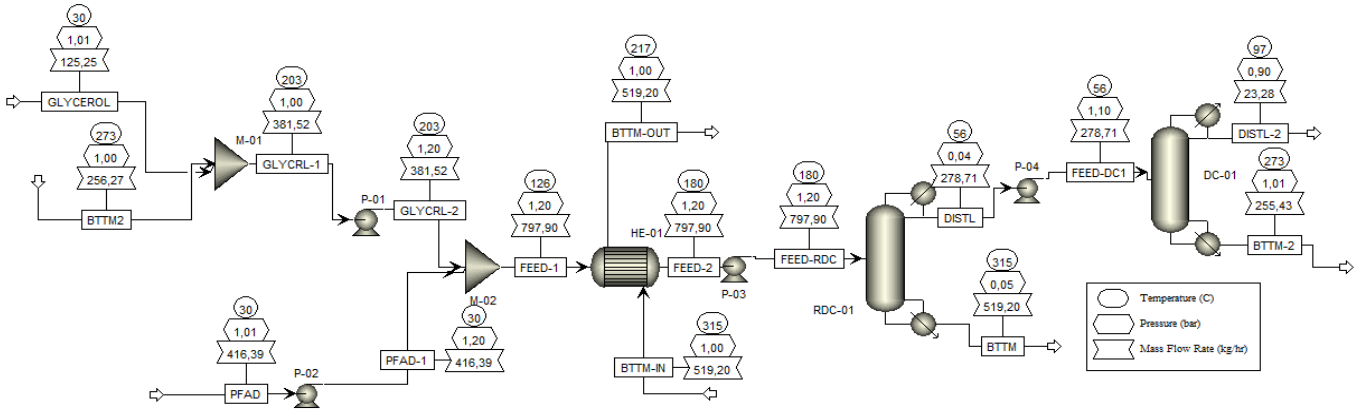

Fig. 6 Calculation result for scenario-1 process flow diagram under vacuum pressure

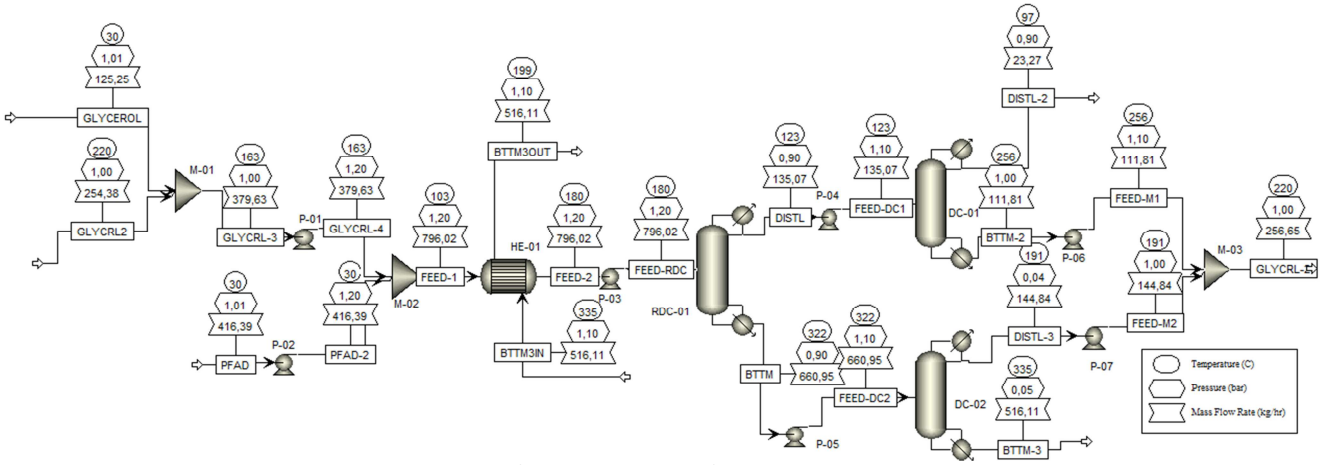

Fig. 7 Calculation result for scenario-2 process flow diagram under vacuum pressure

Simulation results revealed that running the process with a vacuum pressure of 0.05 bar could lower the reaction product temperature to 320^{0}C (Fig. 6 and Fig. 7). Therefore, atmospheric pressure condition is avoided. Summary of the simulation for both scenarios under vacuum condition was shown in Table 3. Preheating process before entering reactive distillation column is carried out using shell and tube heat exchanger with the heat duty of 0,16 Gcal/hr was negligible. This was based on the utilization of the hot reaction product stream as the heating medium. Simulation result also showed that for both scenarios, the most consuming energy equipment was reactive distillation column because of the reboiler's heat duty. Although the Scenario-2 needed more columns than Scenario-1, the Scenario-2 consumed lower energy to yield relatively the same product purity.

IV. Conclusions

Continuous production of monoglycerides in reactive distillation column preferred vacuum pressure to avoid the cracking or the destruction of carbon chain in the monoglycerides. Besides, to have a high purity of monoglycerides, the separation cannot be forced only in the reactive distillation column. Further separation must be conducted separately to purify the monoglycerides (Scenario-2) to have lower energy consumption.

Nomenclature

$kr_{1,4}$	reaction rate constant of monoglycerides formation	$L.mol^{-1}.min^{-1}$
$kr_{2,5}$	reaction rate constant of diglycerides formation	$L.mol^{-1}.min^{-1}$
$kr_{3,6}$	reaction rate constant of triglycerides formation	$L.mol^{-1}.min^{-1}$
K_G	adsorption equilibrium constant of glycerol	$L.mol^{-1}$
C_i	concentration of component *i*	$mol.L^{-1}$
$\hat{u}_v$	maximum allowable vapor velocity based on the gross column cross-sectional area	$m.s^{-1}$
l_t	plate spacing (0.5 – 1.5 m)	m
$\hat{V}_w$	maximum vapor rate	$kg.s^{-1}$

Abbreviations

PFAD	Palm Fatty Acid Distillate
CPO	Crude Palm Oil

Subscripts

G	glycerol
L	linoleic acid
O	oleic acid
ML	monolinolein
DL	dilinolein
TL	trilinolein
MO	monoolein
DO	diolein
TO	triolein

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